<International Research Center for Elements Science>Organotransition Metal Chemistry

International Research Center for Elements Science – Organotransition Metal Chemistry –

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Scope of Research

This laboratory aims to establish new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using experimental methods such as spectroscopy and kinetic techniques, as well as theoretical methods. The research subjects include: 1) development of novel organotransition metal systems for catalysis based on precise ligand design, and 2) preparation of π-conjugated polymers using direct arylation.

KEYWORDS
Transition Metal Complex
Homogeneous Catalyst
Reaction Mechanism
Low-coordinate Phosphorus Ligand
π-Conjugated Polymer

Selected Publications

Chang, Y.-H.; Tanigawa, I.; Taguchi, H.; Takeuchi, K.; Ozawa, F., Iridium(I) Complexes Bearing a Noninnocent PNP-Pincer Type Phosphaalkene Ligand: Catalytic Application to Base-Free N-Alkylation of Amines with Alcohols, *Eur. J. Inorg. Chem.* (in press).

Chang, Y.-H.; Takeuchi, K.; Wakioka, M.; Ozawa, F., C-H Bond Cleavage of Acetonitrile by Iridium Complexes Bearing PNP-Pincer Type Phosphaalkene Ligands, *Organometallics*, **34,** 1957-1962 (2015).

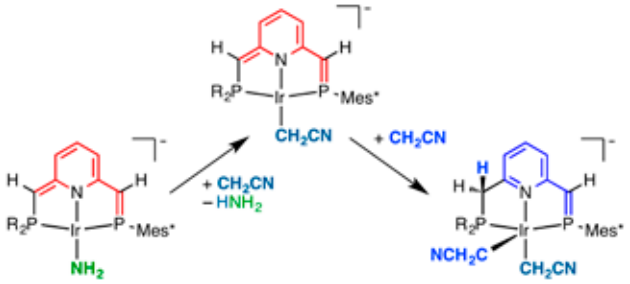
Iizuka, E.; Wakioka, M.; Ozawa, F., Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Synthesis of Donor-Acceptor Polymers with Dithienosilole (DTS) and Thienopyrroledione (TPD) Units, *Macromolecules*, **48,** 2989-2993 (2015).

Taguchi, H.; Chang, Y.-H.; Takeuchi, K.; Ozawa, F., Catalytic Synthesis of an Unsymmetrical PNP-Pincer Type Phosphaalkene Ligand, *Organometallics*, **34,** 1589-1596 (2015).

Wakioka, M.; Nakamura, Y.; Montgomery, M.; Ozawa, F., Remarkable Ligand Effect of $P(2\text{-}MeOC_6H_4)_3$ on Palladium-Catalyzed Direct Arylation, *Organometallics*, **34,** 198-205 (2015).

C–H Bond Cleavage of Acetonitrile by Iridium Complexes Bearing PNP-pincer Type Phosphaalkene Ligands

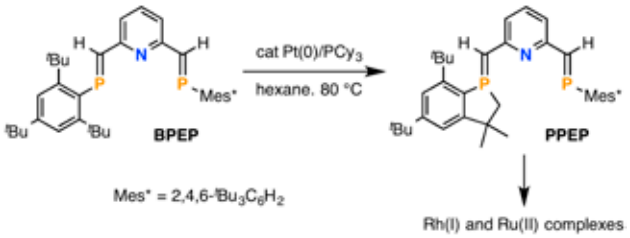
A novel parent amido complex of iridium(I), K[Ir(NH_2)(PPEP*)], coordinated with a dearomatized PNP-pincer-type phosphaalkene ligand (PPEP*) has been prepared by deprotonation with KHMDS from [Ir(NH_2)(PPEP)], with benzophospholanylmethyl and phosphaethenyl groups at the 2,6-positions of pyridine. K[Ir(NH_2)(PPEP*)] has two base points at PPEP* and NH_2 ligands and, thus, successively reacts with two molecules of CH_3CN via heterolytic cleavage of the C–H bond. X-ray structural analysis of the product complex K[Ir(CH_2CN)$_2$(PPEP)] reveals remarkable elongation of the P=C bond, indicative of the occurrence of strong π-back-donation from iridium to PPEP.



Scheme 1. Reaction of [Ir(NH_2)(PPEP)] with acetonitrile.

Catalytic Synthesis of an Unsymmetrical PNP-pincer Type Phosphaalkene Ligand

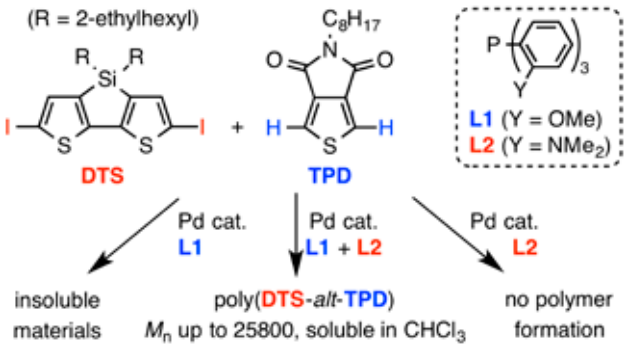
An unsymmetrical PNP-pincer-type phosphaalkene ligand, 2-(phospholanylmethyl)-6-(2-phosphaethenyl)-pyridine (PPEP), has been prepared from 2,6-bis(2-phosphaethenyl)pyridine (BPEP) by intramolecular C–H addition/cyclization of the 2-phosphaethenyl group with a 2,4,6-tri-tert-butylphenyl substituent (CH=PMes*). The reaction proceeds in hexane in the presence of a catalytic amount of [Pt(PCy_3)$_2$] (20 mol %) at 80 °C in a sealed tube, giving PPEP in 32% isolated yield, along with a byproduct of 2,6-bis(phospholanylmethyl)pyridine (BPMP) and a Pt(II) phosphanido complex. The PPEP ligand reacts with [Rh(μ-Cl)(C_2H_4)$_2$]$_2$ and [RuCl_2(PPh_3)$_3$] to afford [RhCl(PPEP)] (**1**) and [RuCl_2(PPh_3)(PPEP)] (**2**), respectively. Complex **1** easily undergoes C–H addition/cyclization at the other CH=PMes* group to afford the 2,6-bis(phospholanylmethyl)pyridine complex [RhCl(BPMP)] (**3**), whereas **2** is stable against C–H addition/cyclization. Treatment of **2** with ^{t}BuOK forms [RuCl(PPh_3)(PPEP*)] (**4**), coordinated with an unsymmetrical PNP-pincer-type phosphaalkene ligand containing a dearomatized pyridine unit (PPEP*).



Scheme 2. Pt(0)/PCy_3 catalyzed C–H addition/cyclization of BPEP to give PPEP.

A Mixed-ligand Approach to Palladium-catalyzed Direct Arylation Polymerization: Synthesis of Donor–Acceptor Polymers with Dithienosilole (DTS) and Thienopyrroledione (TPD) Units

We examined the synthesis of an alternating copolymer with dithienosilole (DTS) and thienopyrroledione (TPD) units via palladium-catalyzed direct arylation polymerization (DArP). Although DArP is attractive as an easy preparation method of π-conjugated polymers without the need for pre-preparation of organometallic monomers, a major problem is that the resulting polymers are occasionally insolubilized in catalytic systems. We have found that the combined use of P(2-$MeOC_6H_4$)$_3$ (**L1**) and P(2-$Me_2NC_6H_4$)$_3$ (**L2**) ligands enables the synthesis of poly(DTS-*alt*-TPD) with good solubility and high molecular weight (M_n up to 25800), and high yield. NMR investigation into the early stage of polymerization revealed two types of side reactions affording structural defects, oxidative coupling (homocoupling) of TPD-H groups and reduction of DTS-I to DTS-H. The combined use of **L1** and **L2** was also effective in preventing these side reactions.



Scheme 3. Synthesis of donor–acceptor polymers with DTS and TPD units via DArP.